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# Simultaneous enhancement of charge transport and exciton diffusion in poly(*p*-phenylene vinylene) derivatives

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Time-resolved luminescence spectroscopy has been used to investigate exciton diffusion in thin films of poly(*p*-phenylene vinylene) (PPV)-based derivatives. Due to chemical modifications the PPV derivatives differ by three orders of magnitude in charge carrier mobility as a result of a reduced energetic disorder. From the photoluminescence decay curves of PPV/fullerene heterostructures, the exciton diffusion coefficient was found to increase by one order of magnitude with decreasing disorder. This increase in the diffusion coefficient is compensated by a decrease of the exciton lifetime, leading to an exciton diffusion length of 5–6 nm for the various PPV derivatives.

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## I. INTRODUCTION

Conjugated polymers have attracted much attention as emissive layers of light-emitting diodes (LEDs) due to their mechanical flexibility and simple and potentially low-cost fabrication.<sup>1</sup> Most of the research has focused on poly(*p*-phenylene vinylene) (PPV) and its derivatives because of their high luminescence efficiencies. It has been demonstrated that by chemical modification the charge transport in PPV can be strongly enhanced.<sup>2</sup> Applying symmetrical side chains leads to a reduction of the energetic disorder and gives rise to an enhanced charge carrier mobility. Such an increase of the charge carrier mobility is beneficial for the operation of a polymeric LED since it lowers the operating voltage of the device, resulting in an increased power efficiency. Photovoltaic devices based on an interpenetrating network of a polymer and a fullerene are another promising application of conjugated polymers.<sup>3–5</sup> In these polymer:fullerene blend devices excitons are created in the polymer phase upon photoexcitation and quenched at the fullerene interface after their diffusion toward the polymer/fullerene heterojunction. The dominating mechanism of exciton quenching is the electron transfer from polymer (donor) to fullerene (acceptor) since energy transfer is inefficient in these systems.<sup>6</sup> After the electron transfer process the resulting bound electron-hole pair at the heterojunction will be dissociated into free carriers and subsequently will be transported to the electrodes.<sup>7</sup> It is clear that an enhanced charge carrier mobility will facilitate this last process, which is beneficial for the solar cell performance. Next to the charge carrier mobility also the exciton diffusion length in a conjugated polymer is an important parameter with regard to the performance of polymer-based photovoltaic devices. The exciton diffusion length limits the polymer domain size in the polymer:fullerene blend and thus puts severe restrictions on the morphology of the active layer.

The charge transport in PPVs has been described by hopping of charge carriers in a Gaussian density of states (DOS). The width of the Gaussian DOS reflects the amount of energetic disorder in the organic semiconductor, and can be di-

rectly obtained from the temperature dependence of the charge carrier mobility.<sup>8</sup> For optical excitations it has been demonstrated that the initial photoexcitation migrates in a disordered organic semiconductor by hopping relaxation within a Gaussian DOS for singlet excitations.<sup>9</sup> In these systems optical transitions have an excitonic character, in contrast to valence band–conduction band transitions in inorganic semiconductors. Although the electronic Gaussian DOS for charge carriers is of a different nature from the optical DOS for singlet excitations, it is important to note that they both reflect the energetic spread in the levels of chain segments due to fluctuations in the conjugation length and structural disorder. It has been demonstrated that the width of the DOS for charge carriers is typically 1.5 times larger than the width for singlet excitation due to inhomogeneous broadening.<sup>8</sup> For device applications an important question is now whether a reduction of the energetic disorder would lead not only to an increased mobility but also to an enhancement of the exciton diffusion. Such a simultaneous enhancement would be beneficial for both the creation of charge carriers in a photovoltaic device as well as their transport to the electrodes. Such a coupling would stress even more the importance of reducing the disorder in these kind of devices.

In steady state the exciton diffusion is characterized by the exciton diffusion length, which is the distance an exciton migrates during its lifetime. The exciton diffusion length has been obtained from the spectral dependence of the photocurrent of polymer/fullerene photovoltaic devices, assuming exciton quenching at the heterojunction only via an efficient short-range electron transfer mechanism.<sup>10,11</sup> A more direct way to study the exciton diffusion and the quenching processes at the interface is to monitor the decay of the photoluminescence from polymer/fullerene bilayer heterostructures.<sup>12,13</sup> The exciton diffusion length can be directly obtained from the variation of the integrated photoluminescence intensity with polymer layer thickness. However, in a recent study it has been demonstrated that intermixing of the polymer and fullerene layers obscures the intrinsic exciton diffusion process.<sup>14</sup> We developed a model system comprising a layer of a polymerizing fulleropyrrolidine with two

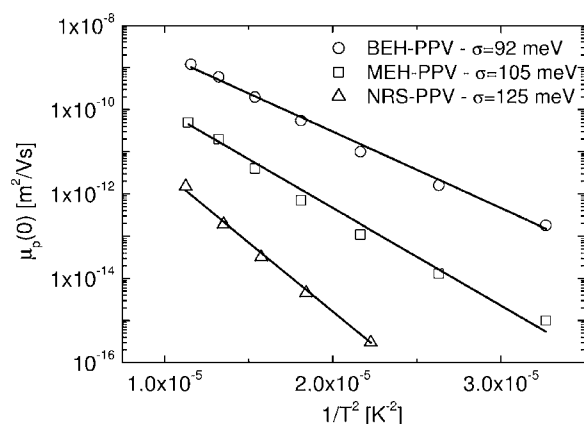


FIG. 1. Temperature dependence  $\ln[\mu_p(0)] \sim 1/T^2$ , obtained from Eq. (1) for the studied polymers.

diacetylene tails (F2D) as acceptor in which the fullerene is immobilized, leading to sharp interfaces. The dynamics of the exciton diffusion is governed by the exciton diffusion coefficient, which can be determined by numerical modeling of the luminescence decay curves.<sup>15</sup> In order to determine an eventual relationship between the charge carrier mobility and exciton diffusion parameters in conjugated polymers, we performed time-resolved photoluminescence quenching measurements in polymer/fullerene bilayers for various PPV derivatives with a varying degree of energetic disorder. We demonstrate that a reduction of the width of the electronic Gaussian DOS from 125 to 92 meV leads to a three-order-of-magnitude enhancement of the charge carrier mobility and simultaneously to a one-order-of-magnitude increase of the exciton diffusion coefficient. The exciton diffusion length, on the other hand, amounts to 6 nm for all PPV derivatives, since the increase of the diffusion coefficient is compensated by a decrease of the exciton lifetime.

## II. EXPERIMENT

The chemical structures of the PPV derivatives studied are shown in the inset of Fig. 2 below. In order to construct a well-defined PPV/fullerene heterostructure, F2D monomers<sup>14</sup> were spin coated from a chlorobenzene solution on top of the glass substrate. After thermo-polymerization of the 40 nm F2D layer during 20 min at 250 °C a film of poly(F2D) was formed, which is proven to be insoluble in most of the common solvents. As a result it can be used for the subsequent spin casting of the polymer layer from a toluene solution. The surface roughness of the cross-linked F2D film after thermopolymerization was characterized with atomic force microscopy and a root mean square (rms) roughness of less than 0.8 nm was determined. The use of poly(F2D) provides a stable and sharp interface,<sup>14</sup> unlike an evaporated C<sub>60</sub> film, where fullerene interdiffusion into the polymer is known to take place leading to ill-defined structures<sup>16</sup> that are unstable in time. Thin films of poly{2-[4-(3',7'-dimethyloctyloxyphenyl)]-co-2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene} (NRS-PPV),

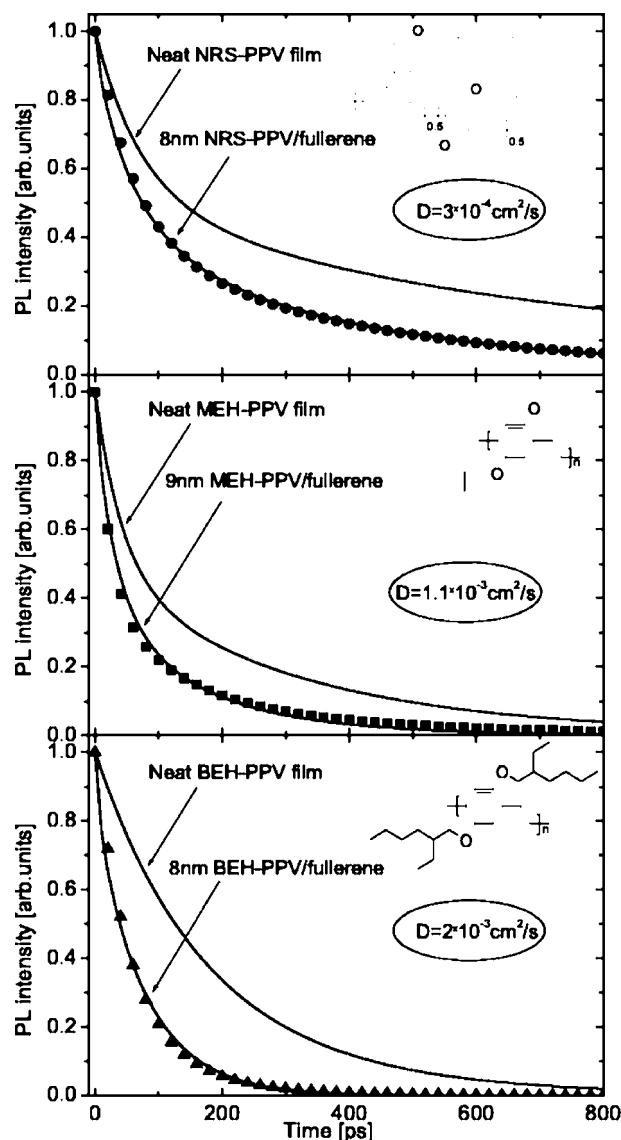


FIG. 2. Deconvoluted and normalized luminescence decay curves for NRS-PPV (●), MEH-PPV (■), and BEH-PPV (▲) for different thicknesses of a polymer film in contact with a poly(F2D) layer. Simulation of these data by Eq. (2) with variable exciton diffusion constant and neat polymer film luminescence decay curves taken as references for each simulation (solid lines).

poly[2-methoxy,5-(2'-ethyl-hexoxy)-*p*-phenylene vinylene] (MEH-PPV), and poly[2,5-bis(2-ethylhexyloxy)-1,4-phenylene vinylene] (BEH-PPV) were prepared by spin-coating the polymers from toluene solution on top of the poly(F2D) film under nitrogen atmosphere. The polymer layer thickness was varied by changing the concentration of the solution and spin speed.

For the analysis of the luminescence measurements it is important that the layer thickness of the conjugated polymer is accurately known. Therefore, two different methods have been employed. First, for the neat conjugated polymer we determined the absorption coefficient at the maximum of the polymer film absorption spectrum by optical density measurements on films of varying thickness.

The film thicknesses of the neat polymer were characterized by surface profilometer and atomic force microscopy (AFM) for thicknesses less than 15 nm. With the relation between absorption and film thickness known we can then determine the thickness of a polymer film on top of the nonabsorbing poly(F2D) layer. Furthermore, AFM measurements showed that the rms of the polymer film and substrate surface roughness did not exceed 1 nm. Second, we measured the total thickness of a polymer/fullerene heterostructure with a surface profilometer. Subsequently, the sample was stored in chlorobenzene for 12 h, thereby removing the conjugated PPV-based polymer. Then the thickness of the remaining poly(F2D) film, being insoluble in chlorobenzene, was measured. By comparing the thickness measurements before and after polymer removal the polymer thickness was determined. The results of the thickness measurements of both methods were mutually consistent. Furthermore, we observed that the films of poly(F2D) and conjugated polymers are smooth and uniform without interfacial voids, which could hinder the determination of the intrinsic exciton diffusion length.

In order to characterize the energetic disorder in conjugated polymers, hole-only diodes were fabricated. On top of a glass substrate with a structured indium tin oxide layer as a hole Ohmic contact, a thin layer of conjugated polymer is spin coated as an active layer, and a gold layer as an electron blocking contact is thermally evaporated. From the space-charge-limited current in these diodes the hole mobility can directly be extracted.<sup>2</sup> The electrical measurements have been carried out with a Keithley 2400 Sourcemeter in a temperature range of 200–300 K under nitrogen atmosphere.

The luminescence quenching due to exciton diffusion and subsequent dissociation at the interface in conjugated polymer/fullerene heterojunctions was monitored by time-resolved photoluminescence spectroscopy. Time-resolved optical experiments were carried out with an output of the mode-locked femtosecond Ti:sapphire laser. Laser pulses were frequency doubled and polymer excitation was performed at 400 nm with *p*-polarized light at 64° incident angle in order to minimize internal reflections. Typical time-averaged excitation intensities on the sample were about 30 mW/cm<sup>2</sup>. Emission was collected at its maximum, 580 nm for all three polymers, normal to the excitation beam. To avoid degradation, samples were sealed under nitrogen in the cell with a quartz window. In time-correlated single-photon-counting (TCSPC) experiments,<sup>17</sup> an instrument response function of 30 ps (full width at half maximum) was used for luminescence decay curve deconvolution. All optical experiments were performed at room temperature.

### III. RESULTS AND DISCUSSION

Current density-voltage (*J-V*) measurements of the hole-only diodes based on three different PPV derivatives were performed to characterize the energetic disorder. The creation of intra- and interchain excitations that

govern the photophysical processes in conjugated polymers films does not allow for a direct determination of the optical Gaussian DOS. Therefore, we take the width of the charge carrier DOS as a measure for the energetic disorder in the PPV derivatives. It has been demonstrated that charge transport in conjugated polymers proceeds by means of hopping in a Gaussian site-energy distribution, which reflects the energetic spread in the transport levels.<sup>12</sup> The hole mobility is described with a three-dimensional transport model in a correlated Gaussian disorder model and is given by the following equation:<sup>12,13</sup>

$$\mu_p(E) = \mu_\infty \exp \left\{ - \left( \frac{3\sigma}{5kT} \right)^2 + 0.78 \left[ \left( \frac{\sigma}{kT} \right)^{1.5} - \Gamma \right] \sqrt{\frac{eEa}{\sigma}} \right\}, \quad (1)$$

where  $\mu_\infty$  is the mobility in the limit  $T \rightarrow \infty$ ,  $\sigma$  is the width of the Gaussian DOS,  $\Gamma$  gives the geometrical disorder, and  $a$  is the average intersite spacing. From the analysis of the temperature-dependent *J-V* characteristics a zero-field mobility is extracted<sup>2</sup> and plotted in Fig. 1 as a function of  $T^{-2}$ .

As shown from Eq. (1) the amount of energetic disorder is directly reflected in the thermal activation of the low-field mobility. From Fig. 1 it can be observed that the hole mobility changes over three decades from  $1.5 \times 10^{-12}$  m<sup>2</sup>/V s for NRS-PPV to  $2 \times 10^{-9}$  m<sup>2</sup>/V s for BEH-PPV. The width of the Gaussian DOS  $\sigma$ , which is a measure of the disorder in the polymer, decreases from 125 to 92 meV for NRS-PPV and BEH-PPV, respectively. NRS-PPV is a random disordered copolymer, which gives rise to stronger structural disorder as compared to the other two polymers and consequently to a larger  $\sigma$ . MEH-PPV is an asymmetric polymer, while BEH-PPV is a more ordered polymer with two symmetric side chains. In comparison with MEH-PPV, the configurational freedom of individual chains in BEH-PPV is limited and results in a decreased energetic spread between the electronic levels of individual chain segments and therefore to a reduced  $\sigma$  for the Gaussian DOS.

The normalized photoluminescence decay curves of the PPV derivatives with and without the fullerene layer, obtained by TCSPC measurements, are shown in Fig. 2. The samples were excited from the polymer side at a wavelength of 400 nm and emission was collected at 580 nm, which corresponds to the maximum of their luminescence spectrum. As expected, the photoluminescence of the polymers in contact with the fullerene decays faster, due to the luminescence quenching by exciton diffusion and dissociation at the PPV/fullerene interface. We model the photoexcitation (exciton) energy distribution  $E(x,t)$  in a polymer film that is in contact with a fullerene layer by using a one-dimensional continuity equation and suitable boundary conditions:



TABLE I. Correlation of charge transport and exciton diffusion parameters with energetic disorder in PPV derivatives.

Polymer	DOS width $\sigma$ (meV)	Exciton diffusion constant $D$ (cm <sup>2</sup> /s)	Hole mobility $\mu$ (m <sup>2</sup> /V s)
NRS-PPV	125	$3 \times 10^{-4}$	$1.5 \times 10^{-12}$
MEH-PPV	105	$11 \times 10^{-4}$	$5.0 \times 10^{-11}$
BEH-PPV	92	$20 \times 10^{-4}$	$2.0 \times 10^{-9}$

$$\frac{\partial E(x,t)}{\partial t} = -\frac{E(x,t)}{\tau} + D \frac{\partial^2 E(x,t)}{\partial x^2} - S(x)E(x,t) + g(x,t),$$

$$\frac{\partial E(0,t)}{\partial x} = 0,$$

$$E(L,t) = 0. \quad (2)$$

Here,  $x$  is the distance from the polymer/nitrogen interface. The first term on the right-hand side of Eq. (2) accounts for the process of radiative and nonradiative decay of the excited states in the neat polymer film with a time constant  $\tau$ . The second term is the one-dimensional exciton diffusion characterized by the diffusion coefficient  $D$ . The dissociation of photoexcitations via electron transfer at the polymer/fullerene interface is represented by the third term. The last term describes the exciton generation process and is proportional to the spatially dependent intensity of the femtosecond laser pulse. In order to find a numerical solution to Eq. (2) we approximate the ultrafast quenching of the excitons at the polymer/fullerene ( $x=L$ ) interface by an infinite quenching rate, represented by  $E(x=L)=0$  with  $L$  the polymer film thickness.

A complication when applying the diffusion model is that the luminescence decay in conjugated polymers cannot be characterized by a single exponential with lifetime  $\tau$ . As a result the model should be modified to include the more complex photoexcitation dynamics of the neat polymer. In our model we implement a time-dependent lifetime  $\tau(t)$  to account for a variety of processes that can lead to such a nonmonoexponential decay. For example, initially photogenerated excitons start to migrate toward defects while relaxing toward lower-energy states. With increasing time it becomes more difficult for the relaxed excitons to migrate, and as a result the lifetime of the exciton increases.<sup>15</sup> Using this approach exciton diffusion constants  $D$  have been deduced from the numerical modeling for the PPV derivatives ranging from  $3 \times 10^{-4}$  to  $20 \times 10^{-4}$  cm<sup>2</sup>/s, as shown in Table I and Fig. 2. It should be noted that the measurement of the luminescence quenching is a relative one, and its result is only weakly dependent on the mathematical description of the decay of the neat polymer luminescence. Another important process that might play a role, especially at longer time scales, is the fact that excitons might be created indirectly by reformation from photogenerated geminate pairs.<sup>18–21</sup> Such a mechanism also leads to a nonmonoexponential decay of the luminescence. We have recently demonstrated for NRS-

TABLE II. Exciton diffusion lengths obtained with the use of time-averaged lifetimes  $\langle \tau \rangle$ .

Polymer	$D$ (cm <sup>2</sup> /s)	$\langle \tau \rangle$ (ps)	$L_D$ (nm)
NRS-PPV	$3 \times 10^{-4}$	1250	6
MEH-PPV	$11 \times 10^{-4}$	455	7
BEH-PPV	$20 \times 10^{-4}$	210	6.5

PPV that when the nonmonoexponential decay of the luminescence is exclusively attributed to this exciton reformation, the exciton diffusion coefficient  $D$  varies only from  $3.0 \times 10^{-4}$  (time-dependent lifetime) to  $4.5 \times 10^{-4}$  cm<sup>2</sup>/s.<sup>15</sup> This analysis provides a measure for the accuracy of the reported exciton diffusion coefficients with regard to the underlying exciton recombination mechanism.

It is demonstrated that an enhancement of the charge carrier mobility of three orders of magnitude is accompanied by an increase of the exciton diffusion coefficient of one order of magnitude, when the energetic disorder is decreased (Table I). Photon absorption in PPV-type and other conjugated polymers creates neutral excitons, which are localized on segments of the polymer chain that are isolated by structural or chemical defects. The excitons migrate via energy transfer to neighboring segments on the same chain or on different chains. It has been demonstrated that the energy transfer in conjugated polymers is mainly of the Förster type.<sup>22</sup> In energetically disordered systems the migration of excitons is accompanied by a relaxation in energy. After photoexcitation the excitons migrate toward lower energies until a localization energy is reached, where the probability of decay becomes larger than the probability to migrate further to lower-energy states.<sup>23</sup> An increased energetic disorder will therefore slow down the migration of excitons, as reflected in the decrease of the exciton diffusion coefficient  $D$ . For efficient exciton dissociation in a photovoltaic device not only the speed at which excitons diffuse is important but also the time that they can diffuse before recombination. The characteristic distance of exciton diffusion in one dimension is the exciton diffusion length

$$L_D = \sqrt{D\tau}. \quad (3)$$

The exciton diffusion length determines the total amount of excitons that are quenched in a polymer film that is in contact with the fullerene layer. In our model we have introduced a time-dependent lifetime to account for the nonexponential decay of the polymer luminescence. The exciton diffusion length can then be estimated by using the time average of the (time-dependent) lifetime.<sup>15</sup> In Table II the time-averaged lifetimes of the different PPV derivatives are given together with the resulting exciton diffusion length. The exciton diffusion length values of typically 6–7 nm are in the same range as earlier reported exciton diffusion length values for other PPV derivatives,<sup>10</sup> and their slight difference is within the experimental error. Apparently,

an integral parameter of the exciton diffusion process, the exciton diffusion length, is not correlated with the energetic disorder and the charge carrier mobility of these PPV derivatives.

However, as discussed earlier the concept of a time-dependent lifetime is not valid in the case of exciton reformation out of photogenerated geminate pairs. Since the independence of the exciton diffusion length on energetic disorder is an important conclusion from our work we want to verify this result by an independent measurement method. The exciton diffusion length as such can be directly determined from steady-state quenching of the time-integrated luminescence.<sup>14</sup> The relative luminescence quenching efficiency  $Q$  is defined as the reduction of the photons emitted from the polymer film in contact with the fullerene layer normalized to the number of emitted photons from the neat polymer film. From this it follows<sup>14</sup> that  $Q$  as a function of the polymer film thickness  $L$  and the exciton diffusion length  $L_D$  is given by

$$Q = \frac{[a^2 L_D^2 + a L_D \tanh(L/L_D)] \exp(-aL)}{(1 - a^2 L_D^2)[1 - \exp(-aL)]} - \frac{a^2 L_D^2 \cosh(L/L_D)^{-1}}{(1 - a^2 L_D^2)[1 - \exp(-aL)]}, \quad (4)$$

under the assumption of an exponential spatial distribution of the excitation energy described by the absorption coefficient  $a$ .

In order to quantify the luminescence quenching efficiency from the time-resolved data, luminescence decay curves for the samples of different polymer film thickness were normalized, and areas under the curves were determined to represent the time-integrated emission. A reduction of the polymer film thickness increases the relative portion of excited states that reaches the polymer/fullerene interface, resulting in an increased relative quenching efficiency  $Q$ . The experimental dependence of  $Q$  on the polymer film thickness is shown in Fig. 3 (symbols) for all three PPV derivatives.

From fitting the relative luminescence quenching efficiency data to Eq. (4) (Fig. 3, solid lines) exciton diffusion lengths of  $5 \pm 1$  nm in NRS-PPV,  $6 \pm 1$  nm in BEH-PPV, and  $6.3 \pm 1$  nm in MEH-PPV are obtained. These values, obtained using steady-state quenching of the time-integrated luminescence,<sup>14</sup> are in agreement with the previous analysis of the time-resolved PL quenching data (Table II). While steady-state relative quenching measurements (Fig. 3) provide direct observation of the exciton diffusion length  $L_D$ , time-resolved approach allows derivation exciton dynamics information.

A possible explanation for the disorder-independent diffusion length would be that the recombination of the excitons is dominated by nonradiative recombination centers in the polymers. In that case the exciton lifetime reflects the time that excitons need to diffuse to these recombination centers. This leads to a constant exciton diffusion length when the different polymers would have an equal amount of nonradiative centers. With an exciton diffusion length of 6 nm this would mean that on average every 12 nm

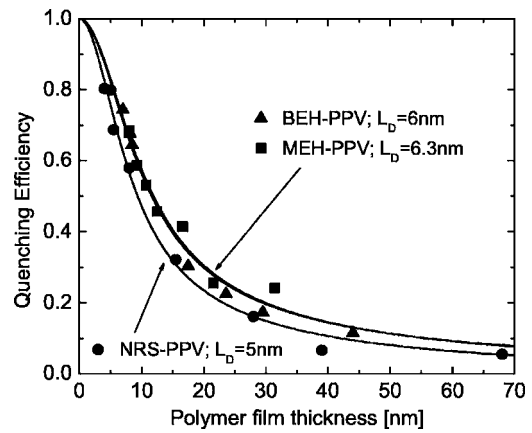


FIG. 3. The relative luminescence quenching in MEH-PPV (■), BEH-PPV (▲), and NRS-PPV (●) for different thicknesses of the polymer film in contact with the poly(F2D) layer. Fitting of these data to Eq. (4) assuming exciton diffusion length ranging from 6.3 nm for MEH-PPV to 5 nm for NRS-PPV is shown by solid lines.

such a center would be present, leading to a typical concentration of  $(12 \times 10^{-9} \text{ m})^{-3} = 6 \times 10^{23} \text{ m}^{-3}$ . Remarkably, this concentration is equal to the amount of electron traps reported for these kinds of polymers, which are suggested to arise from carbonyl groups that also effectively quench excitons.<sup>2</sup> The increase of nonradiative decay is also reflected in the decrease of the photoluminescence efficiency. It decreases from 20% for NRS-PPV to 15% and 9% for MEH-PPV and BEH-PPV, respectively. However, since the luminescence decay is not a single exponential it complicates the direct quantitative coupling between lifetime and PL efficiency.

Furthermore, it has been found that films of asymmetrically substituted PPV derivatives exhibit interconnected ringlike features, which were attributed to ringlike bent chains.<sup>24</sup> Symmetrically substituted PPVs on the other hand did not show these ringlike features but straight rigidlike features. This conformation, as for BEH-PPV, will therefore also increase the interchain contact in the material, resulting in an increase of the interchain energy transfer probability as described in our model by the exciton diffusion constant  $D$ . From studies of MEH-PPV films before and after thermal annealing by near-field scanning optical microscopy<sup>25,26</sup> it has been shown that an increased interchain interaction also promotes the formation of interchain excitonic states that act as quenching centers for mobile excitons.<sup>27,28</sup> This also leads to a reduction of the average lifetime of emissive excitons and is consistent with our observation that an increased exciton diffusion is accompanied by a decrease of the exciton lifetime. Thus, a reduction of the energetic disorder does not appear to be beneficial for the exciton diffusion length, which limits the optimum polymer phase size in photovoltaic devices. Our results demonstrate that the use of polymers with higher charge carrier mobility does not automatically allow larger domains of the polymer phase in bulk-heterojunction solar cells.

#### IV. CONCLUSIONS

We have studied the correlation between energetic disorder and exciton diffusion properties in PPV-based polymer/fullerene heterostructures. By modeling both the time-integrated and time-resolved luminescence quenching the exciton diffusion length as well as exciton diffusion constant were determined. Reducing the energetic disorder by chemical modification of the PPV, giving rise to a charge carrier mobility increase of three orders of magnitude, leads to an enhancement of the exciton diffusion constant of one order of magnitude. The exciton diffusion length is independent of

the amount of energetic disorder, since the increase of the exciton diffusion constant is canceled by a reduction of the exciton lifetime.

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